

**TOUGHENING OF EPOXY RESIN WITH MODIFIED LIQUID  
NATURAL RUBBERS AND ACRYLONITRILE-BUTADIENE LIQUID  
RUBBERS**

By

ABDULALI BASHIR AHMED BEN SALEH

Thesis submitted in fulfilment of the  
requirements for the degree  
of doctor of philosophy

September 2005

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## **Acknowledgements**

By the name of Allah the beneficent and the merciful, all praise and thanks is due to Allah the indivisible creator and sustainer of the world, he can never be praised or thanked enough.

I would like to extend my sincere gratitude to my big family (my parents, brothers and sisters) for their support, dedication and advice. Not forgetting my small family (my wife and daughters) who had constantly given me healthy weather in all aspects of my life study.

I would like to thank my supervisors, Prof. Dr. Zainal Arifin .Mohmed Ishak, Associate Prof. Dr. Azanam Shah Hashim and Associate Prof. Dr. Wan Ahmed Kamil for their continuing support & mentorship in my study. The assistance of Prof. Dr. Umaru S. Ishiaku at the earlier stages of my research is also acknowledged. Acknowledgements are also due to staff and laboratory technician, School of Materials and Mineral Resource Engineering. My respect and thanks are due to all staff and laboratory technician, School of Chemical Science, Universiti Sains Malaysia for their tireless help and cooperation during my research.

I would also like to extend my grateful appreciation and thanks to my colleagues, classmates and friends, for their friendship and support and all postgraduate students of polymer department are also acknowledged.

Finally I would like to thank my sponsor Libyan Government for supporting me with scholarship to continue my postgraduate study.

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## LIST OF ABBREVIATIONS AND MAIN SYMBOLS

a	-	Pre-crack length (mm)
AEP	-	Aminoethylpiperzine
AN	-	Acrylonitrile
ATBN	-	Amine terminated butadiene acrylonitrile liquid rubber
BA	-	Butyl acrylate
CIPS	-	Chemically induced phase separation
CPBER	-	Carboxyl-terminated polybutadiene
CRPEHA	-	Carboxyl randomized poly(2-ethylhexylacrylate) liquid rubber
CTBN	-	Carboxyl terminated butadiene acrylonitrile liquid rubber
CTNR	-	Carboxyl-terminated natural rubber
CTPEHA	-	Carboxyl terminated poly(2-ethylhexylacrylate) liquid rubber
DAC	-	1,2-diaminocyclohexan
DDS	-	Diaminodiphenylsulfone
DGEBA	-	Diglycidyl ether of bisphenol-A
DMA	-	Dynamic mechanical analysis
DPNR	-	Deproteinized natural rubber latex
DSC	-	Differential scanning calorimetry
DVB	-	Divinyl benzene
ELNR	-	Epoxidized liquid natural rubber
ENR	-	Epoxidized natural rubber
EP	-	Epoxy resin

ETBN	-	Epoxy terminated butadiene acrylonitrile liquid rubber
FTIR	-	Fourier transform infrared
$G_{IC}$	-	Critical strain energy release rate
GMA	-	Glycidyl methacrylate
GPC	-	Gel permeation chromatography
HEA	-	2-hydroxyethyl acrylate
HEC	-	2-hydroxyethyl cinnamate
HEMA	-	2-hydroxyethyl methacrylate
HTBN	-	Hydroxyl-terminated butadiene acrylonitrile liquid rubber
HTNR	-	Hydroxyl-terminated natural rubber
IPD	-	Isophorone diamine
IPN	-	Interpenetrating network
KBr	-	Potassium bromide
$K_{IC}$	-	Critical stress intensity factor
KOH	-	Potassium hydroxyl
LCST	-	Lower critical solution temperature
LNR	-	Liquid natural rubber
m	-	Tangent gradient of the initial straight line of load versus deflection curve
Mc	-	Chemical crosslinks
MMA	-	Methyl methacrylate
$M_n$	-	Number average molecular weight
$M_w$	-	Molecular weight
$M_z$	-	Z average molecular weight

NaOH	-	Sodium hydroxide
NCOPBER	-	Isocyanate-terminated polybutadiene
NR	-	Natural rubber
P	-	Maximum load
P(B-S)	-	Poly butadiene-co-styrene
PAEK	-	Polyaryletherketones
PDMS	-	Poly (dimethyl siloxane)
PEI	-	Poly (etherimides)
PEK	-	Poly(etherketone)
PES	-	Poly(ethersulfone)
PMMA	-	Poly methyl methacrylate
pph	-	Parts per hundred
PPO	-	Polyphenylene oxide
PSF	-	Polysulfone
PU	-	Polyurethane
RRIM	-	Rubber Research Institute Malaysia
RT	-	Room temperature
S	-	Span length
SEM	-	Scanning electron microscopy
SEN-B	-	Single edge notched specimens in three points bending
St	-	Styrene
t	-	Specimen thickness
TELNR	-	Telechelic epoxidized liquid natural rubber

$T_g$	-	Glass transition temperature
TGMDA	-	Tetraglycidyl methylenedianiline
TLNR	-	Telechelic liquid natural rubber
TPNRs	-	Thermoplastics natural rubber
TPU	-	Thermoplastic polyurethane
UCST	-	Upper critical solution temperature
VBGE	-	vinylbezyl ether
w	-	Specimen width
Y	-	Geometrical factor
ZnSe	-	Zinc selenide
$\Delta G_m$	-	Free energy of mixing
$\Delta H_m$	-	Enthalpy of mixing
$\Delta T_m$	-	Entropy of mixing

## ABSTRACT

The preparation of liquid natural rubber (LNR) by depolymerizing deprotonized natural rubber latex was carried out. Similarly, the preparation of epoxidized liquid natural rubber (ELNR) was also undertaken. FTIR and NMR spectroscopis were used to determine the structures of LNR and ELNR and to calculate the epoxidation levels in LNR and ELNR chains. Both LNR and ELNR show the presence of hydroxyl and carbonyl end functional groups. Because of the epoxidation process, ELNR has a higher degree of epoxidation i.e., 25 mol % compared to 8.5 mol% for LNR.

LNR and ELNR and two liquid commercial rubbers i.e., ETBN and CTBN were evaluated as toughening agents in an epoxy (DGEPA)-hardener (IPD) system. The four liquid rubbers were evaluated at 5, 10, 15, and 20 phr. The reactivity, thermal, mechanical and morphology properties of the liquid rubbers-EP-IPD systems were evaluated. The fracture toughness was evaluated at three different speeds i.e., 1, 100 and 500 mm/min.

A general and similar trend was observed for all liquid rubbers; the gel and cure times increased with increasing of rubber content. The gel and cure temperatures for all the liquid rubbers modified EP are higher than those of the unmodified EP. The glass transition temperatures ( $T_g$ ) of the modified EP were found to decrease with increasing rubber content. Generally, the tensile strength and Young's modulus decreased with increase in rubber content followed by increment in tensile strain. The flexural strength and modulus of modified EPs are generally lower than those of the unmodified one. However, the fracture toughness of the EP was observed to improve in the presence of the

liquid rubbers. The toughening effect became more apparent as the testing speed was increased. Fracture surface analysis by scanning electron microscopy (SEM) revealed the presence of a two-phase morphology for all the four liquid rubber-EP systems. The rubbery phase was distributed as rubber particles within the epoxy matrix.

The gel time for ELNR-EP at 5-15 phr was shorter (4.3 to 4.4) min than for LNR-EP (5.0 to 5.4) min. The cure temperature of the ELNR-EP was between 138-143 °C which are higher than those of the LNR-EP (124-141 °C). ELNR-EP, over the range of rubber loading investigated, has a particle size distribution ranging from 0.2 to 1.88  $\mu\text{m}$  which is much smaller than that of LNR-EP with a distribution ranging from 5 to 10  $\mu\text{m}$ . The reactivity and the particle size distribution results indicate that ELNR is more compatible with EP than LNR. Thus, ELNR-EP, overall, displays higher tensile strength, strain at break, and flexural strength than LNR-EP.

At 5 and 10 phr, LNR and ELNR did not give significant improvement in the fracture toughness when compared with ETBN and CTBN. However, at 15 and 20 phr, both LNR and ELNR were found to be good toughening agents for EP giving significant improvement in the  $K_{IC}$ , which can be considered quite comparable to ETBN and CTBN depending on the test speeds. Also at 15 and 20 phr, both LNR and ELNR give better overall tensile and flexural properties compared to ETBN and CTBN.

# **PENGLIATAN RESIN EPOKSI DENGAN GETAH ASLI CECAIR TERUBAHSUAI DAN GETAH CECAIR AKRILONITRIL-BUTADIEN**

## **ABSTRAK**

Getah asli cecair (LNR) disediakan dengan cara penyahpempolimeran penyahprotinan lateks getah asli ternyahprotin. Getah asli cecair terepoksida (ELNR) juga disediakan dengan cara yang hampir sama. Spektroskopi FTIR dan NMR telah digunakan untuk mengenalpasti struktur LNR dan ELNR dan menentukur peringkat pengepoksidaan dalam rantaian LNR dan ELNR. Kedua-dua LNR dan ELNR menunjukkan kehadiran kumpulan-kumpulan berfungsi hujnng hidroksil dan karbonil. Disebabkan oleh proses pengepoksidaan, ELNR mempunyai darjah pengepoksidaan yang lebih tinggi iaitu 25 mol % berbanding 8.5 mol % untuk LNR.

LNR, ELNR dan dua getah cecair komersial iaitu ETBN dan CTBN dikaji sebagai agen pengliatan dalam sistem epoksi (DGEPA)-pengeras (IPD). Empat getah cecair tersebut dikaji pada 5, 10, 15 dan 20 psg. Sifat keupayaan tindak balas, terma, mekanik dan morfologi bagi sistem getah cecair-EP-IPD telah dikaji. Keliatan rekahan ( $K_{IC}$ ) telah dikaji pada tiga kelajuan ujian yang berbeza iaitu 1, 100 dan 500 mm/min.

Satu kelakuan yang umum dan hampir sama telah diperhatikan untuk semua getah cecair. Masa penggelan dan pematangan telah meningkat dengan peningkatan kandungan getah. Suhu penggelan dan pematangan bagi semua EP terubahsuai getah cecair adalah lebih



tinggi berbanding getah cecair tidak terubahsuai. Suhu peralihan kaca ( $T_g$ ) bagi EP terubahsuai getah cecair didapati menurun dengan peningkatan kandungan getah. Amnya, kekuatan tensil dan modulus Young didapati menurun dengan peningkatan kandungan getah diikuti oleh peningkatan dalam terikan tensil. Kekuatan fleksural dan modulus EP terubahsuai getah cecair didapati lebih rendah berbanding sistem tidak terubahsuai. Walau bagaimanapun, keliatan rekahan didapati telah meningkat dengan kehadiran getah cecair. Kesan pengeliatan menjadi lebih ketara dengan peningkatan kelajuan ujian. Analisis permukaan rekahan dengan mikroskop imbasan elektron (SEM) menunjukkan kehadiran morfologi dua fasa untuk kesemua empat sistem getah cecair-EP. Fasa bergetah telah tersebar sebagai partikel getah dalam matriks epoksi.

Masa penggelan untuk ELNR-EP pada 5-15 psg adalah rendah (4.3 hingga 4.4) minit berbanding LNR-EP (5.0 hingga 5.4) minit. Suhu pematangan bagi ELNR-EP adalah di antara  $138 - 143\text{ }^{\circ}\text{C}$  yang mana ia lebih tinggi berbanding LNR-EP ( $124 - 141\text{ }^{\circ}\text{C}$ ). Merangkumi julat beban getah yang dikaji, ELNR-EP mempunyai taburan saiz partikel di antara 0.2 hingga 1.88  $\mu\text{m}$ , yang mana ia lebih kecil berbanding LNR-EP yang mempunyai taburan saiz di antara 5 – 10  $\mu\text{m}$ . Keputusan keupayaan tindak balas dan taburan saiz partikel menunjukkan bahawa ELNR adalah lebih serasi dengan EP berbanding LNR. Maka, secara keseluruhannya, ELNR-EP mempamerkan kekuatan tensil, terikan takat putus dan kekuatan fleksural yang lebih tinggi berbanding LNR-EP.

Pada 5 dan 10 psg, LNR dan ELNR tidak memberikan peningkatan yang ketara dalam keliatan rekahan berbanding ETBN dan CTBN. Namun begitu, pada 15 dan 20 psg, kedua-dua LNR dan ELNR telah didapah menjadi agen pengeliatan bagi EP yang memberikan

peningkatan  $K_{IC}$  yang signifikan yang mana ia dikira agak setanding dengan ETBN dan CTBN bergantung kepada kelajuan ujian. Juga pada 15 dan 20 psg, kedua-dua LNR dan ELNR secara keseluruhan memberikan sifat tensil dan fleksural yang lebih baik berbanding ETBN dan CTBN.

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

أَقْرَأْ بِاسْمِ رَبِّكَ الَّذِي خَلَقَ ﴿١﴾ خَلَقَ الْإِنْسَانَ مِنْ عَلَقٍ ﴿٢﴾ أَلْقِمْ وَرَبُّكَ  
الْأَكْرَمُ ﴿٣﴾ الَّذِي عَلَّمَ بِالْقَلَمِ ﴿٤﴾ عَلَّمَ الْإِنْسَانَ مَا لَمْ يَعْلَمْ ﴿٥﴾

سُورَةُ الْعَلَقِ

*[96:1-5] Read! In the name of your Lord who created - Created the human  
from something which clings. Read! And your Lord is Most Bountiful -  
He who taught (the use of) the Pen, Taught the human that which he  
knew not.*

*Chapter 96: AL-ALAQ*

## CHAPTER ONE

### INTRODUCTION

#### 1.1 Overview

Epoxy resins (EPs) constitute one of the most important classes of thermosetting polymers, and have been extensively used as high performance adhesive composite materials, due to their outstanding mechanical and thermal properties such as high modulus, and tensile strength, low creep, high glass transition temperature, high thermal stability, and moisture resistance, (May and Tanaka 1973). In the cured state, EPs are brittle materials that have fracture energies of about two orders of magnitude lower than engineering thermoplastics and other high performance materials (Bascom and Huston 1989). To retain their position as materials of choice for many applications such as adhesives and composite matrixes, epoxies should be modified to improve their properties such as fracture toughness.

One of the most successful methods to toughen EPs is the incorporation of rubber phase into the brittle epoxy matrix, which may be achieved by the use of reactive liquid rubber (Reiw, *et al.* 1996) or preformed rubber particles (Lin, and Shieh 1998). The rubber used for toughening of EP is generally a butadiene-acrylonitrile copolymer with reactive functional end groups such as carboxyl, amine or epoxy, i.e., CTBN, ATBN, or ETBN (Kunz, *et al.* 1980; Butta, *et al.* 1986). Rubber can be dissolved in an epoxy matrix as a plasticizer or flexibilizer, and/or separated from the matrix as a second phase during the curing process. The rubber, which is either, dissolved in the epoxy matrices or as a dispersed as second a phase, can significantly affect the fracture properties of the blends.

Many efforts have been made to understand the behavior of the dispersed rubber phase, which separates from the resin before gelation. Sultan and McGarry (1986) found that toughening mechanisms are affected by the rubber particle sizes. Pearson and Yee (1986) studied elastomer modified epoxies with respect to their mechanical properties, crosslink density and mechanism of toughening. Evaluation of effective crosslink density of matrix resin, measurement of glass transition temperature  $T_g$ , cure characterization through differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) of diglycidyl ether of bisphenol -A (DGEBA) modified with carboxy terminated butadiene acrylonitrile (CTBN) liquid rubber have also been reported by Kalfoglou, *et al.* (1973) and Pearson, *et al.* (1989). While Qian, *et al.* (1995) studied the synthesis and application of core-shell rubber particles as toughening agents for epoxies.

An attempt to toughen the EP using a polyurethane (PU) prepolymer as modifier via interpenetrating network (IPN) grafting has also been reported (Harani, *et al.* 1998). The PU prepolymer has been synthesized based on hydroxyl-terminated polyester resins and used as modifier for EP at different concentration. Ratna and Banthia (2000) showed that carboxyl terminated poly(2-ethylhexylacrylate) (CTPEHA) liquid rubber can be used as an impact modifier for EP cured with an ambient temperature hardener. However, carboxyl terminated oligomers can only be synthesized by bulk polymerization, which is difficult to control. Hong and Chan (2004) have studied the effect of epoxidized natural rubber (ENR) on the curing behaviors and adhesive strengths of an epoxy (DGEBA) and dicyandiamide/2-methyl imidazole system.

The functional groups of the rubber form chemical bonds with the epoxy matrix to providing interfacial bonds between the matrix and the dispersed phase. The initial rubber composition should not exceed about 20 % by weight to be most effective (Bascom, Houston 1989). This assures an increase in toughness without sacrificing the good properties of the EP. Most researchers would now agree an improvement in toughness whilst minimizing any deterioration in other important properties/ parameters such as modulus and  $T_g$ , phase separation, followed by the gradual development of a two phase morphology, is critically important. In order to achieve this outcome, the rubber must be dissolved and become dispersed on a molecular level in the epoxy, but required to precipitate out when epoxy crosslinking occurs. Under these circumstances the required two-phase morphology will develop with the formation of rubbery particles dispersed in and bonded to the crosslinked epoxy matrix. Thus elements of both initial compatibility and eventual incompatibility must be regarded as vital elements of the system (Collyer, 1994).

The mechanical and physical properties of the final product depend on the crosslink density, rubber compositions and glass transition temperatures in both dispersed and continuous phases, the volume fraction, as well as the number and size, of the dispersed particle phase. Cure conditions for a single formulation can vary all of these parameters. The majority of curing agents employed in EP systems provide a substantial contribution to the properties of the crosslinked products. Thus the choice of curing agent can therefore be of critical importance and need to be considered carefully. This is particularly true for rubber-modified formulations where curing agents can influence many factors capable of contributing to the final properties of the cured product. These can include its influence on

epoxy rubber compatibility and morphology, epoxy rubber chemistry, rate of cure and epoxy crosslink density (Collyer, 1994).

## **1.2 Problem statement**

As some of the most widely used thermoset materials, EPs have special chemical characteristics compared with other thermosetting resins: no byproducts or volatiles are formed during curing reactions, so shrinkage is low; EPs can be cured over a wide range of temperatures; and the degree of cross-linking can be controlled. Depending on the chemical structure of the curing agents and on curing conditions, the properties of cured EPs are versatile, including excellent chemical and heat resistance, high adhesive strength, low shrinkage, high strength and hardness, and high electrical insulation (Shell Development Company, 1983). But cured epoxy systems have one main drawback: their considerable brittleness, which shows poor fracture toughness, typically below  $1.0 \text{ MPa}\cdot\text{m}^{1/2}$  (Pearson and Yee, 1989), poor resistance to crack propagation, and low impact strength (Lee and Neville, 1967). This inherent brittleness has limited their application in fields requiring high impact and fracture strengths, such as reinforced plastics, matrix resins for composites, and coatings. Therefore, in the last few decades, much attention has been paid to improve the thermal and mechanical properties of EPs, especially making them tough.

It is widely believed that the brittleness of EPs is associated with their highly cross-linked structures (Min, *et al.* 1993 and Scherzer, 1994). So most of the researches have been focused on improving the relatively poor fracture properties of EPs, either by reducing the

crosslinked density of the epoxy network or by modifying commercially available EPs with secondary components. This study will focus on the second approach, i.e., modifying EPs by using commercially reactive liquid rubber (CTBN and ETBN) and synthesized liquid natural rubber (LNR) and epoxidized liquid natural rubber (ELNR) to improve the toughness of the EPs. The liquid natural rubbers prepared are different in the terms of chemical structures, hence they are considered as modified natural rubbers. The presence of end functional groups and epoxy groups in the structure of liquid natural rubbers are to be compatible with EP, hence they are considered as modifiers of EP.

### **1.3 Objectives of the study**

The main objectives of the study are:

1. To prepare/synthesize liquid natural rubber (LNR) and epoxidized liquid natural rubber (ELNR) and to characterize both the liquid rubbers.
2. To incorporate both LNR and ELNR into epoxy system as toughening agent and study their effect on the thermal, mechanical and morphology properties of EP.
3. To minimize the use of the more expensive modifiers EP and replacing LNR, ELNR with other EP modifiers, this would not only generate interest in terms of cost, but would also create a new approach to the EP modifiers, whereby one gets to choose a custom-made compound that is suitable for their specific needs and budget.
4. To investigate the effect of two types of commercial liquid rubbers i.e., epoxy terminated butadiene-acrylonitrile co-polymer (ETBN) and carboxyl terminated butadiene-acrylonitrile co-polymer (CTBN) and study their effects on the thermal,



mechanical and morphological properties of EP. To compare their effect with LNR and ELNR effect on the mechanical properties of EP.

#### **1.4 Outline of thesis structure**

Chapter one provides a brief introduction to EPs followed by some fundamentals on the definition and classification of EPs modifiers. Issues of concern, which generated the ideas and motivation to perform this research work, are also stated. The objectives and the general flow of the whole research program are also carefully outlined.

Chapter two relates the role of polymer matrix (EPs), hardeners (crosslinking agents), toughening agents and extenders with particular interest focused on toughening EPs. Subsequently, a literature survey was done on various published works on toughening of EP and preparation of liquid natural rubber, particularly those that are closely related to this work.

Chapter three describes the step by step the experimental procedures employed, materials used, details of laboratory equipments which were used as well as any other processing techniques involved in generating any data that were employed during the course of the study.

Chapter four reports on the results and discussion of this study which are divided into seven parts. Part1 deals with FTIR and NMR spectra that were used to determine the structures of LNR and to determine and calculate the epoxidation level of LNR. Molecular

weights and glass transition temperatures measurements of LNR are reported. Part 2 reports the effect of the liquid natural rubber (LNR) as a toughening agent on the mechanical, thermal and morphological properties of modified EP. Data, graphs and charts on the mechanical and thermal properties of the LNR modified EP are presented. Reactivity and FTIR analysis are also reported. The morphology of the fracture surface was studied using scanning electron microscopy (SEM) and was related to the numerical data obtained. Part 3 reports the preparation of ELNR using solution and latex methods, and deals with FTIR and NMR spectra that were used to determine the structures of ELNR and to determine the epoxidation levels of ELNR. Molecular weights and glass transition temperatures measurements of ELNR are presented. Part 4, 5 and 6 report the effect of ELNR, CTBN and ETBN respectively as toughening agents on the mechanical, thermal and morphological properties of modified EP. Part 7 compares all the liquid rubbers in terms of their effect on the properties of EP.

Chapter five presents some concluding remarks on the present work as well as some suggestions for future work.

## **CHAPTER TWO**

### **BACKGROUND AND LITERATURE REVIEW**

#### **2.1 Thermosetting polymer**

All polymers can be divided into major groups based on their thermal processing behavior. Those polymers that can be heat-softened in order to process into a desired form are called thermoplastics. Waste thermoplastics can be recovered and refabricated by application of heat and pressure. Polystyrene is an important example of a commercial thermoplastic. In comparison, thermosets are polymers whose individual chain have been chemically linked by covalent bonds during polymerization or by subsequent chemical or thermal treatment during fabrication. Once formed, these crosslinked networks resist heat softening, creep, and solvent attack, but cannot be thermally processed. Such properties make thermosets suitable material for composites, coating, and adhesive applications. Principal examples of thermosets include epoxy, phenol-formaldehyde resin, and unsaturated polyesters (Fried, 1995).

Some of the reasons that thermosets are often used as composite structural materials are derived from their abilities to consolidate the different components due to their initial low viscosity, and also their high glass transition temperatures and good dimensional stability under stress due to their network structure after being cured. All these latter properties are due to their network structure. During the crosslinking reaction (cure), the reactive monomers grow in molecular weight (MW) to form branched structures and eventually

interlink to form the three-dimensional network thus the crosslink reaction is only performed when polymer are formed. In these cases, the polymerization occurs first, and then the crosslink reaction will occur between incipient molecules (Billmeyer, 1984; Mark, *et al.* 1989). In order to form such a three-dimensional network, some of the reactant molecules must have more than two functional groups per molecule in order to initiate branching in the polymerization. The variation of chemical structure during the cure is represented in Figure 2.1.

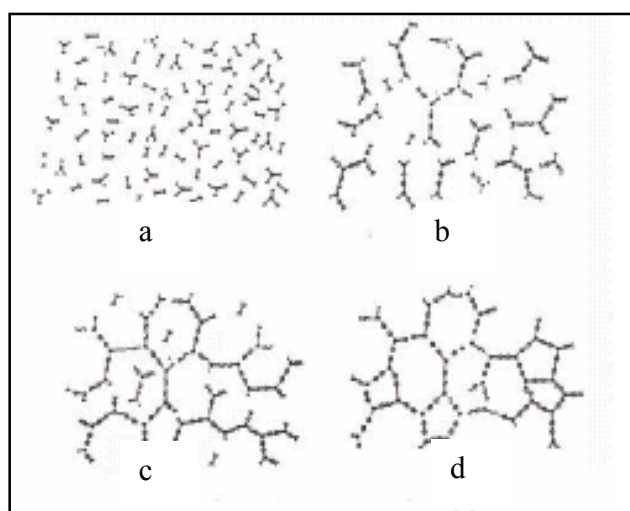


Figure 2.1: Schematic 2-D representation of thermoset formation: a) A-stage, partially polyfunctional monomer; b) B-stage, linear and branched materials below gel point; c) Incipient state of gel, gelled but incompletely crosslinked network with significant sol fraction; d) Fully cured C-stage thermoset (Billmeyer, 1984).

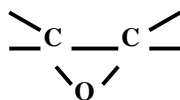
One of the important parameter that are used to characterize a crosslinked polymer other than those that are used for the thermoplastic polymers is the crosslink density, or, equivalently, the molecular weight between chemical crosslinks,  $\langle M_c \rangle$ . This parameter is strongly related to their physical and mechanical properties. Generally, high crosslink density, or low  $\langle M_c \rangle$ , yields high rigidity, strength, solvent resistance and possibly

improved thermo-oxidative stability. However, highly crosslinked networks exhibit restricted molecular mobility, which often translates into undesirable brittleness, low strains to failure, poor impact properties and poor fracture toughness. One of the advantages of thermosets resin is that they are liquid or easy to become liquid when the process begins. This allows for easy mixing of colorants, fillers, reinforcements and processing aids. Moreover the low viscosity of thermosets at the beginning of the process has advantages of being moldable into very complex shapes and capable of wetting the reinforcement fibers in composite fields (Pascault, *et al.* 2002).

The useful thermosets polymer from a historical standpoint and for industrial applications include phenol-formaldehyde networks (resols and novolacs), unsaturated polyesters, epoxy networks cured with diamines, acids, or anhydrides, polyurethane, polyurea, amino resins (formaldehyde with urea, melamine or acrylic), acetylene derivatives, silicones, polyimides, cyanates and vulcanization of unsaturated hydrocarbons (Mark, *et al.* 1989).

## 2.2 Epoxy resins (EPs)

EPs are characterized by a three-membered ring known as the epoxy, epoxide, oxirane, or ethoxline group as show below:



Commercial EPs contain aliphatic, cycloaliphatic, or aromatic backbones. The capability of the epoxy ring to react with a variety of substrates imparts versatility to the resins.

Treatment with curing agents gives in-soluble and intractable thermoset polymers. In order to facilitate processing and modify cured resin properties, other constituents may be included in the compositions: filler, solvents, diluents, plasticizers, and accelerators. EPs were first introduced commercially in 1949 and are now used in a wide variety of industries. They were used in protective coatings and structural applications such as laminates and composite, tooling, molding, casting, construction, bonding and adhesives. EPs have high chemical and corrosion resistance, good mechanical and thermal properties, outstanding adhesion to various substrates, low shrinkage upon cure, flexibility, good electrical properties, and ability to be processed under a variety of conditions. In 1936, De Trey Freres produced a low melting bisphenol-A-based EP, which gave a thermoset composition with phthalic anhydride (Adams and Gannon 1985).

EPs are prepared by the reaction of compounds containing an active hydrogen group with epichlorohydrin followed by dehydrohalogenation with presence of a stoichiometric amount of NaOH (Figure 2.2), or by direct epoxidation of olefins by peracids. The most important intermediate in EP technology is the liquid reaction product of excess epichlorohydrin and bisphenol A, which can be described as the crude diglycidyl ether of bisphenol A (DGEBA) (Adams and Gannon 1985) where the degree polymerization is nearly zero ( $n = 0.2$ ):

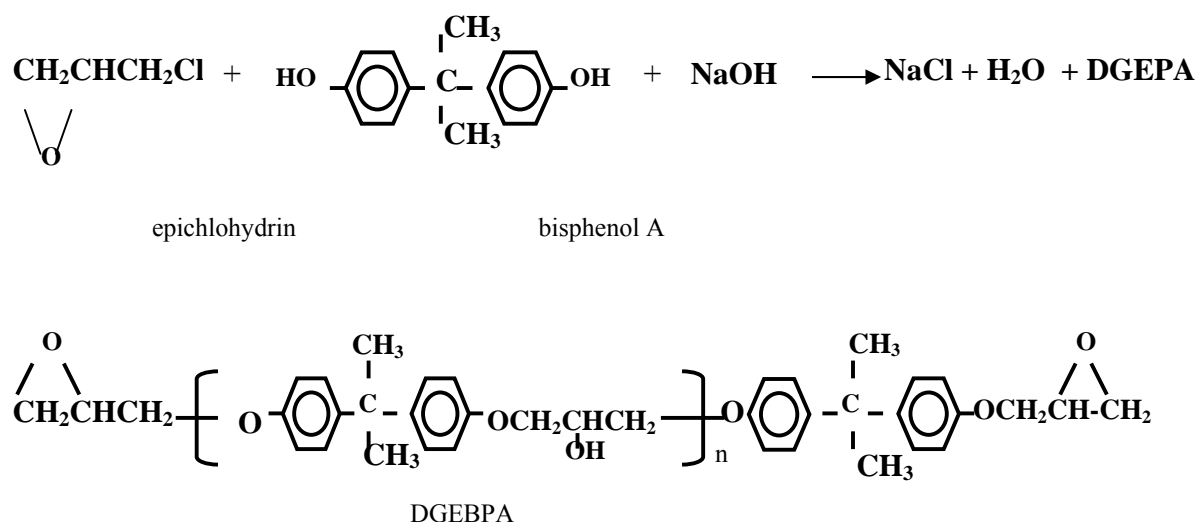


Figure 2.2: Reaction of preparation of diglycedyl ether of bisphenol A (DGEPA).

In response to more stringent quality requirements, liquid resins of higher purity, i.e., higher monomer content, are produced with fewer side reactions. In a typical laboratory preparation of a liquid EP, epichlorohydrin and methyl cellosolve (monomethyl ether of ethylene glycol) as solvents are charged to a four-neck round-bottom flask equipped with mechanical stirrer, reflux condenser, dropping funnel, and thermometer. Bisphenol A is added under agitation. The mixture is heated to 55-60°C, and pulverized sodium hydroxide is added for 3 hours at the same temperature. After a 30 minutes holding period, the temperature is lowered to 50-55°C and the epichlorohydrin -water mixture distilled under reduced pressure with a gradual temperature rise over four hours to 120°C. The reaction mixture is cooled to 110°C, treated with water to remove salt, thoroughly agitated, and allowed to separate into layers; washing is repeated. Warming to 140°C under reduced pressure for 30 minutes removes the remaining volatiles. Filtration yields the final product, EP. Pure DGEPA is a solid with a melting point of 43°C (Adams and Gannon. 1985 and Brydson, 1995).

Unmodified liquid resins are widely used in castings, tooling, and adhesives and coatings applications. Unmodified liquid resins are used for the preparation of modified resins and as starting material for higher molecular weight EPs.

#### 2.2.1 Curing of epoxy resins

The choice of resin and curing agent (hardener) depends on the application and on handling characteristics (viscosity, pot life, gel time), curing temperature and time, use properties (mechanical, chemical, thermal, electrical), toxicological and environmental limitations; and cost. A wide variety of curing agents can be used to cure EPs and there are many ways in which they can be classified (Adams and Gannon, 1985). A description of curing agents is shown below:

##### 2.2.1.(a) Amine hardening systems

Amine curing agents will crosslink epoxide resins either by a catalytic mechanism or by bridging across epoxy molecules. In general, primary and secondary amines act as reactive curing agents whilst the tertiary amines are catalytic. Primary and secondary amines are the most widely used curing agents for EPs (Brydson, 1995). The reaction between amines and an EP (Figure 2.3) is shown as follows:



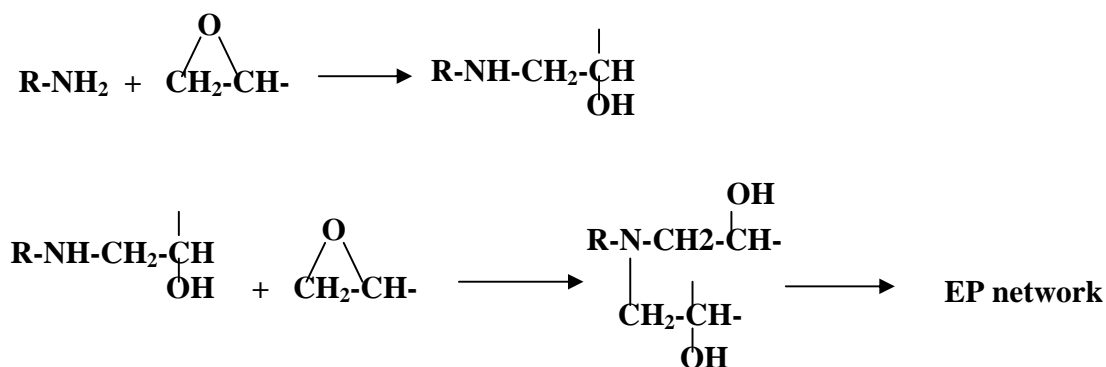


Figure 2.3: The reaction between amines and an EP

Reaction of an epoxy group with a primary amine initially produces a secondary alcohol and a secondary amine, which in turn, reacts with an epoxy group to give a tertiary amine and two secondary hydroxyl groups. Initial curing with a secondary amine produces a tertiary amine and a secondary alcohol. However, with excess epoxy, the secondary hydroxyl groups formed gradually add to the epoxy groups (Adams and Gannon, 1985).

Aliphatic amines give good room temperature (RT) cures with DGEBA - type Visine. Aliphatic amines do not react with cycloaliphatic resins at room temperature, but require high temperatures and accelerators such as tertiary amines (Adams and Gannon, 1985 and Brydson, 1995).

Cycloaliphatic amines were developed in Europe, where their use as epoxy curing agents is well established. Unmodified cycloaliphatic amines require elevated temperatures. They cure quickly and have excellent color stability, low viscosity, and good chemical resistance. They are however more expensive than other types of curing agents. N-Aminoethylpiperzine (AEP), Isophorone diamine (IPD), and 1,2-Diaminocyclohexan (1,2-

DAC) are the principal commercial cycloaliphatic polyamine curing agents (Adams and Gannon, 1985 and Brydson, 1995).

Polyamides are extremely versatile curing agents, they are inexpensive, have little color, and can be mixed in any ratio. They provide good mechanical properties, exhibit readily workable pot lives, and cure under mild conditions. They are mainly used in coating formulations (Adams and Gannon, 1985 and Brydson, 1995).

Amidoamines have all the properties of polyamides, except for a significantly lower viscosity; they are prepared by the reaction of tall-oil fatty acid with a multifunctional amine (Adams and Gannon, 1985 and Brydson, 1995).

Theoretically, a crosslinked thermosets polymer structure is obtained when equivocal quantities of resin and curing agent are combined. The stoichiometric quantity of amine used to cure an epoxy is a function of equivalent weight per active hydrogen of an amine and the epoxide equivalent weight of EP and it is expressed as follows (Adams and Gannon, 1985 and Brydson, 1995).

:

$$m = \frac{\text{equivalent weight per active hydrogen}}{\text{epoxide equivalent weight}} \times 100 \quad (2.1)$$

Where m is by weight amine per 100 parts by weight EP

### 2.2.1.(b) Anhydrides hardening systems

Numerous structurally different anhydrides can be used as epoxy curing agents. Epoxy-anhydride systems exhibit low viscosity, long pot life, low exothermic heats of reaction, and little shrinkage when cured at elevated temperatures. The cure system exhibits good mechanical and electrical properties and is used in filament wound epoxy pipe and electrical cabling applications. Anhydride cured formulations exhibit better thermal stabilities than similar amine cured systems. Anhydrides are the principal curing agents for cycloaliphatic and epoxidized olefin resins. Three types of anhydride may be recognized, room temperature solids, room temperature liquids and chlorinated anhydride, e.g. phthalic anhydride, malic anhydride, and chlorendic anhydride. The anhydrides are usually used at ratios of 0.85:1.1 moles anhydride carboxyl group per epoxy equivalent (Brydson, 1995).

## 2.3 Toughened plastics

Most plastics designed for engineering applications are multiphase materials that contain elastomeric impact modifiers and often other polymers. The addition of toughening agents usually increases not only the overall ductility of the polymer over a wide temperature range but also improves resistance to notch sensitivity and toughness of sections and reduces water absorption, etc. As more knowledge of miscibility, compatibility and interaction of polymers has become available in recent years, more varied approaches to improved polymer blends have become apparent. Simultaneous with this, there has been an explosion of activity in the field of toughened engineering plastics. Many new tough polymer blends based on polyamides, poly (phenyleneoxide), polyesters and polycarbonates have been introduced in large volume applications, particularly in the automotive industry (Juran, 1989).

Engineering polymers, which are most frequently rubber toughened, include poly-amides, polyesters, EPs, poly (phenyleneoxide), polycarbonates and polyacetyls. Combinations of engineering polymers have been found to be useful in applications requiring high strength, high heat deformation temperatures solvent resistance and toughness (Collyer, 1994).

### 2.3.1 Toughened Thermosets

Most of the novel thermosets resins developed over the last decade are largely used as matrices in fiber reinforced composites for aerospace industries. These new resins are capable of withstanding elevated temperature applications via increasing rigidity and/ or crosslink density of their networks. However, in almost every case the same network, which provides the high temperature properties, also inhibits molecular flow thus rendering the material low in toughness. Consequently, there is a lot of interest in the toughening of these thermosets (Folkes and Hope, 1993; Brydson, 1995).

The fracture toughness of thermoset resins is lower than thermoplastics. However, by incorporating toughener into the thermoset resins such as epoxies, the level of toughness can be brought into line with some thermoplastics. Much of the published work concerning toughening of thermosetting resins involves the incorporation of soft elastomeric substances into the resin matrix. (Folkes and Hope, 1993).

Initial attempts to improve ductility or impact strength for epoxy thermoset systems employed various levels of “reactive ” or “non-reactive plasticizers” based on long chain epoxidized glycols and dimer acids (Lee and Neville, 1967). However, the use of most of these modifiers reduced thermal stability and strengths. Traditional toughness modifiers

such as carboxyl terminated butadiene acrylonitrile copolymer rubbers (CTBN) have been widely used to improve toughness since the frontier work by Sultan and McGary (Riew, *et al.* 1976). However, such improvements were achieved at the expense of high temperature performance. This has been attributed to the low glass transition temperature of the unsaturated rubbery phase that lowers the end-use temperature and the modulus of the resulting networks. The amount of rubber incorporated is limited to the maximum of about 20 % wt for this reason. A binary phase morphology consisting of relatively small (0.1- 5 mm) rubbery particles dispersed in and bonded to epoxy is generated.

The toughness of the resulting networks was influenced by the properties of the pure epoxy (cross link density), morphology of dispersed particle phase, levels of interfacial adhesion, the initial composition and properties of the toughener. (Riew, *et al.* 1976). Significant improvements (10 folds or so) for fracture toughness ( $K_{IC}$ ) have been reported only in the case of lightly crosslinked epoxies (Pearson and Yee, 1993). Even though extensive studies have been done on the rubber toughened or thermoplastic toughened thermosets, the primary cause for the improvement of fracture toughness for the modified thermosets has not been firmly established due to the experimental difficulties to control the factors independently.

Siloxane elastomers provide an attractive alternative to the butadiene acrylonitrile elastomers often used for modification of epoxy networks. Poly(dimethyl siloxane) (PDMS) displays interesting properties; such as good thermal stability, weatherability, oxidative stability and moisture resistance. The non-polar nature and the low surface energy of PDMS drive thermodynamically the siloxane phase to migrate to the air-polymer

interface. This sometimes occurs even in the case of chemically crosslinked microphase separated systems. Such a migration of the siloxane phase leads to the formation of a hydrophobic and chemically bound surface coating. Therefore, this ‘slippery’ surface layer enhances the friction and wears properties (i.e., decreases friction and wear) of the epoxy substrate (Yorkgitis, *et al.* 1984).

Particulate fillers such as alumina, silica, glass, dolomite, aluminum hydroxide and zirconia have also been investigated with limited success (Moloney, *et al.* 1983; Spanoudakis, and Young, 1984). Hybrid systems like glass fillers in rubber modified epoxies and zirconia-rubber-epoxy systems have also been reported to enhance toughness (Kinloch, *et al.* 1985). The use of thermoplastic polymers as toughener for thermosets has become widely employed in attempts to improve the fracture toughness as well as high thermal and dimensional stability. Studies using non-reactive thermoplastic modifiers have not always indicated the significant improvement of the toughness. It may be due to poor adhesion between the thermoset matrix and the modifier phase or others. It has been demonstrated that the selection of a thermoplastic as a toughener is limited to a few reactive thermoplastic polymers that exhibit high toughness, ductility, and  $T_g$ . Improvements in toughness along with the retention of the moderately high modulus and thermal stability have been reported in the case of polysulfone modified epoxy and bismaleimide networks (Hedrick, *et al.* 1985; Liptak, *et al.* 1991; Winkinson, *et al.* 1993; Pak, *et al.* 1993).

### 2.3.2 Toughening of epoxy resins

EPs are considered to constitute one of the most important classes of thermosetting polymers, which have been used extensively as high performance adhesive composite materials, due to their outstanding mechanical and thermal properties such as high modulus, and tensile strength, low creep, high glass transition temperature, high thermal stability, and moisture resistance (May and Tanaka, 1973). In the cured state EPs are brittle materials that have fracture energies some two orders of magnitude lower than modern thermoplastics and other high performance materials (Rezaifard, *et al.* 1993). To retain their position as materials of choice for many applications of adhesives and composite matrixes, epoxies should be modified to improve their properties such as fracture toughness.

One of the successful methods to toughen EPs is the incorporation of rubber phase into the brittle epoxy matrix, which may be achieved by the use of reactive liquid rubber or preformed rubber particles (Reiw, *et al.* 1996). Butadiene-acrylonitrile copolymers with reactive functional end groups (CTBN, ETBN and ATBN) are widely used as toughening agents. The rubber is initially miscible with the epoxy but during the polymerization the rubber particles phase separate due to slight immiscibility with the matrix. At the appropriate concentration of rubber, the dispersed rubber phase can improve the toughness without a significant decrease in the other properties of epoxies (Pearson and Yee, 1993). The improved toughness of rubber-toughened epoxies has been proposed through three mechanisms; crazing, shear banding and elastic deformation of rubber partials. These mechanisms can either act alone, or in combination, to produce toughening effect (Sayre, *et al.* 1994).

Many efforts have been made to understand the behavior of toughening EPs. McGarry and co-workers in 1973 were among the first researchers to investigate the behavior of rubber toughened EP and suggested the toughening mechanism involving generation of crazes and shear banding in the vicinity of rubber particles (Hunston, *et al.* 1984). Methods of preparing EPs capable of being cured at room temperature to yield adhesives of high shear and peel strengths are examined. The preferred formulation consists of reacting the diglycidyl ether of bisphenol A with a dicarboxy-terminated butadiene-acrylonitrile (CTBN) rubber (10–15 phr). These materials may be cured with diethyleneglycol bis-propylamine to yield adhesives, which have shear and peel strengths of about 32 MN/m<sup>2</sup> and 5 KN/m respectively at 10 phr CTBN and about 26 MN/m<sup>2</sup> and 8 KN/m at 15 phr CTBN (Paul, *et al.* 1977).

One of the important methods in rubber toughened EP is the addition of either a carboxyl- or amine- terminated butadiene-acrylonitrile copolymer as shorted CTBN and ATBN, respectively. These two rubber toughened EPs imparted the desirable properties, improve the fracture properties with a minimal decrease in other mechanical properties. However, the relatively high glass transition temperature of acrylonitrile-butadiene copolymer limit their low temperature flexibility (Okamoto, 1983). The other method to toughen EPs is reactive polybutadiene toughened epoxy, that can replace butadiene-acrylonitrile copolymer, but the systems and conditions for modification of EP with function polybutadiene have not been definitely optimized yet (Mijovic, *et al.* 1984). Mechanical properties (impact strength,  $K_{IC}$ , elastic modulus and hardness) of ATBN/DGEBA blends of various compositions, cured at different temperatures, have been investigated. Both homogeneous and heterogeneous materials, with different properties, have been obtained.



ATBN has been shown to be ineffective if a massive phase separation does not occur. Maximum toughness, measured by  $K_{IC}$ , is obtained in the 120°–140°C cure temperature range.

Scanning electron microscopy (SEM) micrographs of impacted specimens described that the moving cracks go through the segregated particles and suggest they lack ductility. The improvement in fracture resistance also depends on modifications of matrix properties (Levita *et al.* 1985). The DGEBA epoxies toughened by various levels of several types of carboxyl terminated copolymers of butadiene-acrylonitrile (CTBN) liquid rubber are studied. The materials are deformed in uniaxial tension and in three-point bending with an edge notch. Scanning electron microscopy of fracture surfaces indicates cavitation of the rubber particles to be a major deformation mechanism. Particle-particle interaction is also found. Optical microscopy of thin sections perpendicular to the fracture surface shows that the cavitated particles generate shear bands.

The toughening effect is hypothesized to be due to cavitation, which relieves the triaxial tension at the crack tip, and shear band formation, which creates a large plastic zone (Pearson and Yee, 1986). Acrylic elastomers with pendant epoxy groups were used to reduce the brittleness of bisphenol-A diglycidyl ether EP. The elastomers were prepared by copolymerization of butyl acrylate (BA), vinylbenzyl glycidyl ether (VBGE) and styrene (St) or acrylonitrile (AN). These terpolymers were effective for the toughening of the EP system. The addition of 20 wt % of the terpolymer (74 mol% BA, 18 mol% VBGE and 8 mol% St) resulted in an 80% increase in the fracture toughness ( $K_{IC}$ ) of the cured resin at a slight expense of its mechanical properties. The modified EPs had two-phase

morphology in which the volume fraction and average diameter of the dispersed elastomer particles were dependent on the structure and concentration of the terpolymer (Takao, *et al.* 1990).

The morphology of a system consisting of a bisphenol A diglycidylether (DGEBA) based epoxy, cured with a cycloaliphatic diamine (4,4' primediamino-3, 3' primedimethyldicyclohexymethane, 3DCM), in the presence of an epoxy-terminated butadiene-acrylonitrile random copolymer (ETBN), was studied as a function of the cure schedule and the initial rubber concentration. The type of mechanical test and strain rate did not affect SEM results. Trends observed for the particle size distribution, the volume fraction of dispersed phase, the concentration of dispersed phase particles and the composition of both phases as a function of polymerization temperature and rubber concentration, were discussed. A correlation between the viscosity at the cloud point and the average size of dispersed phase particles was found for different systems, independently of the cure temperature and the initial rubber amount (Verchere, *et al.* 1991).

A series of blends have been prepared by adding a polyetherimide, in varying proportions, to a trifunctional EP, triglycidylparaaminophenol, cured with 4,4'-diaminodiphenylsulphone. All the materials showed two-phase morphology when characterized by dynamic mechanical thermal analysis and scanning electron microscopy. Addition of the thermoplastic resulted in improved fracture properties ( $K_{IC}$  and  $G_{IC}$ ), as measured by three-point bending experiments, although no obvious correlation with blend morphology was observed (Hourston and Lane, 1992). Chen and Hourston (1992) studied the miscibility and fracture behaviour of an EP-bisphenol-A polycarbonate blend. Samples

of neat EPs based on Epikote 828 cured with diethylenetriamine and blends containing 10 wt% of a polycarbonate were prepared at 20°, 40° and 70°. The critical stress intensity factor ( $K_{IC}$ ) and critical strain energy release rate ( $G_{IC}$ ), the morphology and glass transition temperatures ( $T_g$ ) were examined with a three-point bending test, scanning and transmission electron microscopy and dynamic mechanical analysis, respectively. The results show that the blend is miscible and that  $K_{IC}$  and  $G_{IC}$  increase somewhat on the addition of the polycarbonate.

Polyphenylene oxide (PPO) was found to be miscible in diglycidyl ether of bisphenol A (DGEBA) based epoxy. The PPO-DGEBA system exhibited upper critical solution temperature (UCST) behavior. The cloud point temperatures were measured and found to be sensitive to the molecular weight of the EP. A series of PPO-modified epoxies were cured with piperidine at 160 °C, which is above the cloud point temperature. Upon curing, two-phase solids were formed, which contained discrete PPO particles. However, the two-phase particulate morphology was not uniform and numerous large, occluded PPO particles were observed. In order to improve the uniformity, several styrene-maleic anhydride copolymers were evaluated as potential surfactants for PPO-DGEBA blends. The formation of a uniform, particulate morphology was facilitated by the addition of a styrene-maleic anhydride copolymer, containing a 10:1 ratio of styrene to maleic anhydride. According to Pearson *et al* (Pearson *et al.* 1993), this is the first time that an emulsifying agent has been added to improve the morphology of thermoplastic modified epoxies to the best their knowledge. On the other hand, Poly(methylmethacrylate)-grafted-natural rubber has been studied as a novel toughening agent for EP systems based on diglycidyl ether of bisphenol A (Shell Epikote 828), both in bulk and as an adhesive.